

Research Article

Studies on AC Electrical Conductivity of CdCl_2 Doped PVA Polymer Electrolyte

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PVA-based polymer electrolytes were prepared with various concentrations of CdCl_2 using solvent casting method. Prepared polymer films were investigated using line profile analysis employing X-ray diffraction (XRD) data. XRD results show that the crystallite size decreases and then increases with increase in CdCl_2 . AC conductivity in these polymer increases films first and then decreases. These observations are in agreement with XRD results. The highest ionic conductivity of $1.68 \times 10^{-8} \text{ Scm}^{-1}$ was observed in 4% of CdCl_2 in PVA polymer blend. Crystallite ellipsoids for different concentrations of CdCl_2 are computed here using whole pattern powder fitting (WPPF) indicating that crystallite area decreases with increase in the ionic conductivity.

1. Introduction

There is a continued interest in conducting polymers due to their properties like easy fabrication, low cost, leak proof, biodegradability, and good storage capacity. Conducting polymers find application in the development of advanced high energy electrochemical devices for example, batteries, fuel cells, electrochemical display devices, and photoelectrochemical cells. The development of conducting polymers involves several approaches: (i) dry solid state polymers, (ii) gel/plasticizer polymer, and (iii) composite polymer. Many lithium-based polymer electrosystems have been investigated earlier [1]. In our study we have chosen poly vinyl alcohol (PVA) as a host polymer doped with cadmium chloride (CdCl_2) for preparing polymer electrolytes. PVA is a water soluble polymer and has several interesting physical properties. PVA is having a good charge storage capacity and dopant-dependent electrical and optical properties [2, 3]. PVA is a semicrystalline polymer. Cadmium chloride is a white crystalline compound. It is a hygroscopic solid that is soluble in water. Cadmium chloride is also used for photocopying, dyeing, and electroplating.

The present study focused on the AC electrical conductivity of PVA doped with CdCl_2 blends which will be an

interesting study for being used as a final product in some technical applications like electrochemical applications, fuel cells, batteries, electrochemical display devices, and photoelectrochemical cells. The present study is also concerned with the correlation between crystallite ellipsoids and conductivity in CdCl_2 -based polymer films. An explanation in terms of C–O and C–H bond stretching using FTIR data has been made in this paper. FTIR spectra are useful in identifying the change in functional groups due to the presence of cadmium ions. Cadmium ions have a tendency to break polymer network because of its reasonable positive charge behaviour which is indicated in our FTIR studies.

2. Experimental

2.1. Sample Preparation. Poly vinyl alcohol (PVA) was purchased from Loba Chemie, Mumbai, India, and was used without further purification. CdCl_2 was purchased from M/s SD fine chemicals, Bangalore, Karnataka, India. The polymer films were prepared by solvent casting method [4] for various concentrations of salt. The films were dried at room temperature for at least 7 days. The thicknesses of the films were 10 microns.

TABLE 1: Microstructural parameters of CdCl_2 doped with PVA polymer using exponential distribution function.

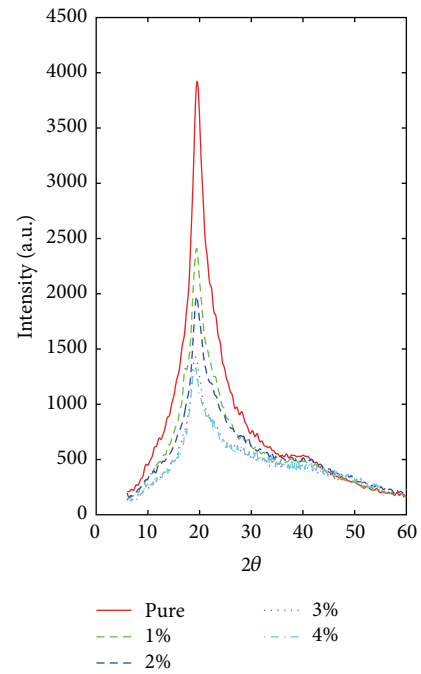
Samples	Bragg's reflections (hkl)	2θ (Deg)	g (%)	Surface density (S)/(nm) ²	$\langle N \rangle$	D_s (nm)	α	Delta	Crystallite area (nm ²)
Pure	(012)	19.56	1.35	4.47	3.9	1.76	0.52	$2.11E - 3$	1.39
	(321)	41.56	1.35	2.14	3.65	0.79	0.73		
1%	(021)	19.40	1.35	4.51	4.05	1.85	0.47	$2.39E - 3$	1.32
	(114)	38.48	1.35	2.30	3.07	0.71	0.89		
2%	(012)	19.56	1.35	4.47	4.17	1.88	0.45	$3.13E - 3$	1.16
	(321)	41.46	1.35	2.14	2.85	0.61	1.24		
3%	(021)	19.24	1.35	4.54	3.66	1.68	0.56	$3.12E - 3$	1.07
	(114)	38.54	1.35	2.30	2.75	0.64	1.33		
4%	(021)	19.02	1.5	4.60	3.94	1.83	0.52	$2.07E - 3$	1.20
	(311)	37.24	1.5	2.38	2.73	0.65	1.20		

2.2. X-Ray Diffraction Recordings. X-ray diffraction patterns of the polymer films were recorded using Rigaku MiniFlex II Diffractometer with Ni filtered $\text{CuK}\alpha$ radiation of wavelength 1.5406\AA and a graphite monochromator. The specifications used for the recordings are 30 kV and 15 mA. The polymer films were scanned in continuous mode in the 2θ range of 5° – 60° with a scanning speed of $5^\circ/\text{min}$ and step size of 0.02° .

2.3. AC Conductivity and FTIR Measurement. The AC conductivity of these polymer films was measured using Hioki (Japan) model 3532–50 computer interfaced digital LCR meter in the range of 50 Hz–5 MHz. The infrared spectra of these polymer films were recorded at room temperature in the (wave number) range of 4000 cm^{-1} to 400 cm^{-1} using JASCO FTIR 4100 type A spectrometer.

3. Results and Discussion

3.1. X-Ray Diffraction Studies. X-ray diffraction analysis is a very useful method in determining the microstructure of the material. The microstructural parameters like crystal size ($\langle N \rangle$) and lattice strain (g) in polymer films were investigated by line profile analysis [5]. These studies also emphasize upon the importance of line profile analysis [6] and suggest that single-order method is a reasonably good approach to obtain microstructural parameters [7, 8]. The XRD pattern of pure PVA and CdCl_2 complexed PVA films is shown in Figure 1. From Figure 1, we observe a Bragg peak at $2\theta = 19.56^\circ$. In salt added films, the intensity of the peak is found to decrease and width increases. This indicates that the addition of CdCl_2 salt causes a decrease in the degree of crystallinity of the polymer PVA up to a certain concentration and then increases. A casual glance at Table 1 indicates that the crystallite area decreases by 23% with the addition of CdCl_2 salt. This suggests that on the complementary side amorphous region has increased. This decrease is due to the amorphous nature of the film. The correlation between the intensity of the peak and the degree of the crystallinity is established by Hodge et al. [9]. We have developed in-house program for computation of crystallite size and lattice strain by simulating the whole powder pattern fitting and the details of the procedure are given in our earlier paper [10]. The simulated whole powder patterns

FIGURE 1: XRD pattern of pure PVA and (PVA + CdCl_2) polymer films.

of these polymer electrolytes are given in Figure 2. These microstructural parameters are given in Table 1. It is evident from Table 1 that crystallite size is different in different Bragg directions. Recently Leonardi et al. have remarked that the crystallite size is different along different Bragg angles [11]. In order to get a better perspective and understanding of these microstructural parameters, we have used cell parameters of PVA reported earlier [12] to plot unit cell crystallite shape using all the reported (hkl) reflections. With this crystallite which has a centre, we have plotted crystallite size (D in nm) for the two Bragg reflections (012) and (321) in Figure 3 which is not drawn to scale. This figure indicates the crystallite size and shape along various Bragg directions. Furthermore a lattice strain (g in %) given in Table 1 implies that a distance of D in nm along a direction perpendicular to Bragg plane results in a change in lattice spacing of this percentage.

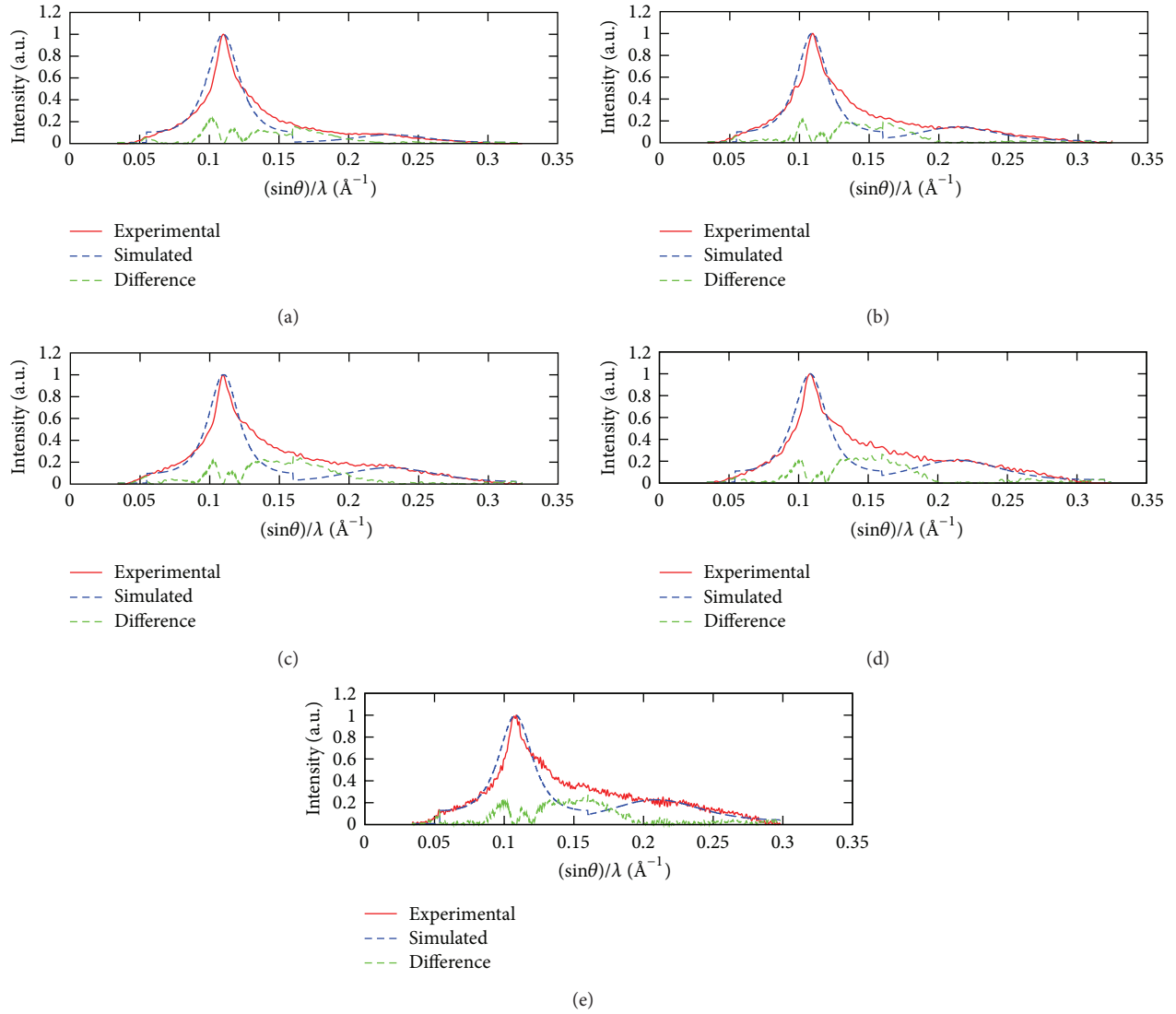


FIGURE 2: Experimental and simulated profiles using whole powder pattern fitting method.

With this understanding, we have projected the variation in crystallite size along different Bragg directions onto a plane for various CdCl_2 doped PVA polymer electrolytes which is given in Figure 4. It is evident from Figure 4 that the crystallite area decreases with increase in concentrations of CdCl_2 [13]. In Table 1, $\langle N \rangle$ indicates average number of unit cells counted in a direction perpendicular to the Bragg plane participating in the scattering process which is relatively small compared to perfect crystals. Furthermore, Table 1 also indicates that S (number of atoms/area = d_{hkl} /volume of the unit cell) increases on an average with the concentration of CdCl_2 for both the Bragg reflections. Alpha given in Table 1 determines the width of the crystallite distribution function used to simulate the whole powder patterns for these polymer electrolytes.

3.2. AC Conductivity and FTIR Analysis. The measured conductance $G(\omega)$ from 50 Hz to 5 MHz was used to

calculate the AC conductivity of the sample using the relation

$$\sigma = \frac{G(\omega) d}{A}, \quad (1)$$

where $G(\omega)$ is the measured conductance, A is the area of the sample, and d is the thickness of the sample. The variation of AC conductivity as a function of frequency for PVA composition of (PVA + CdCl_2) polymer electrolyte is shown in Figure 5. From Figure 5, it is observed that conductivity increases with increase in frequency. The increase in AC conductivity is due to increase in the composition of the salt in polymer matrix resulting in relatively more number of free ions. This will increase the mobile charge carriers as observed in Table 2. These charge carriers move in the amorphous polymer matrix and hence the conductivity increases. Thus there is a relation between the amorphous nature of the polymer film and the conductivity. In general, conductivity

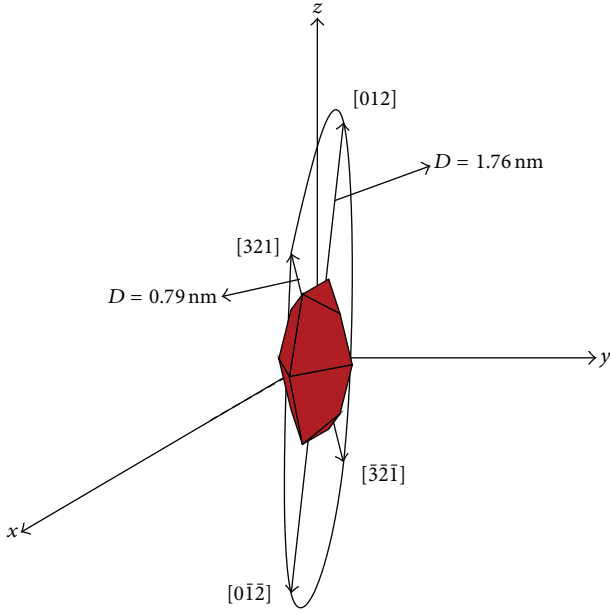


FIGURE 3: Unit cell crystallite shape and crystallite size along different Bragg angles.

TABLE 2: Microstructural parameters of CdCl₂ doped PVA films.

Sample	Crystallite size (D_s in Å)	Conductivity (Scm^{-1})
Pure PVA	1.76	$2.26E - 10$
	0.79	
1% CdCl ₂	1.85	$5.36E - 9$
	0.71	
2% CdCl ₂	1.88	$7.22E - 9$
	0.61	
3% CdCl ₂	1.68	$0.375E - 9$
	0.64	
4% CdCl ₂	1.83	$1.63E - 8$
	0.65	

increases as the degree of crystallinity decreases, as observed above, which is the compliment of increase in amorphous nature [14].

The recorded FTIR spectra are shown in Figure 6. From IR spectra, we have considered a few prominent bands around 3450 cm^{-1} which correspond to O-H stretching of the hydroxyl groups of PVA. Around 1200 cm^{-1} the bands corresponds to stretching of C-O groups. For pure PVA, the fundamental and first overtone transition of C-O bonds is centered at 1994 cm^{-1} and 3830 cm^{-1} , respectively. The nature of chemical bonds in polymers can be studied through the characterization of the vibration modes by infrared spectroscopy [15]. The equilibrium vibration frequency of this bond is calculated using the following relations [16].

Frequency of the fundamental transition = 1944 cm^{-1}

$$= \bar{\nu}_e - 2\chi_e \bar{\nu}_e. \quad (2)$$

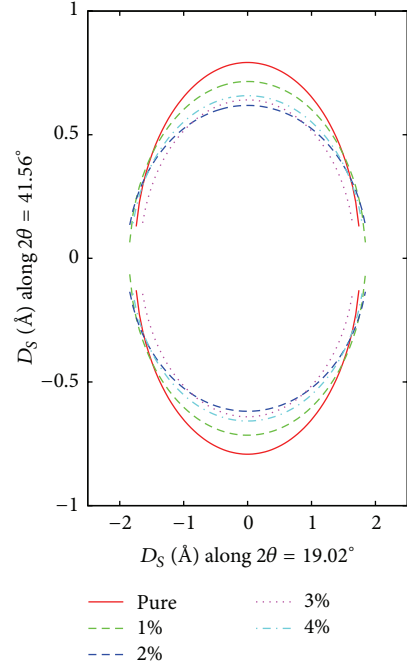


FIGURE 4: Crystallite ellipsoids in (PVA + CdCl₂) based polymer films. 1out: 1% CdCl₂, 2out: 2% CdCl₂; 3out: 3% CdCl₂; 4out: 4% CdCl₂; pureout: pure PVA.

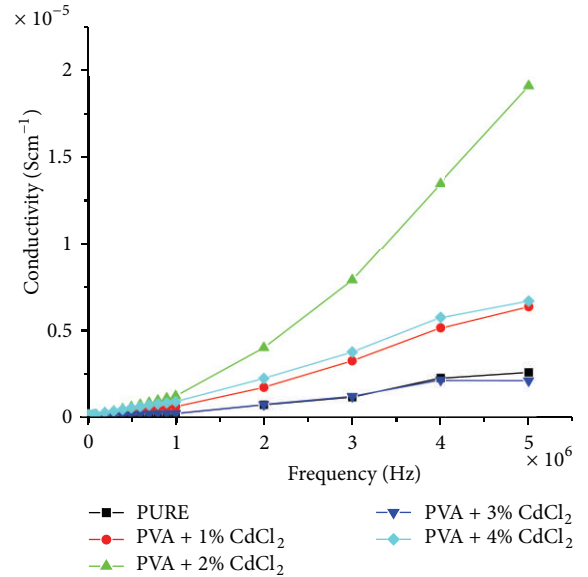


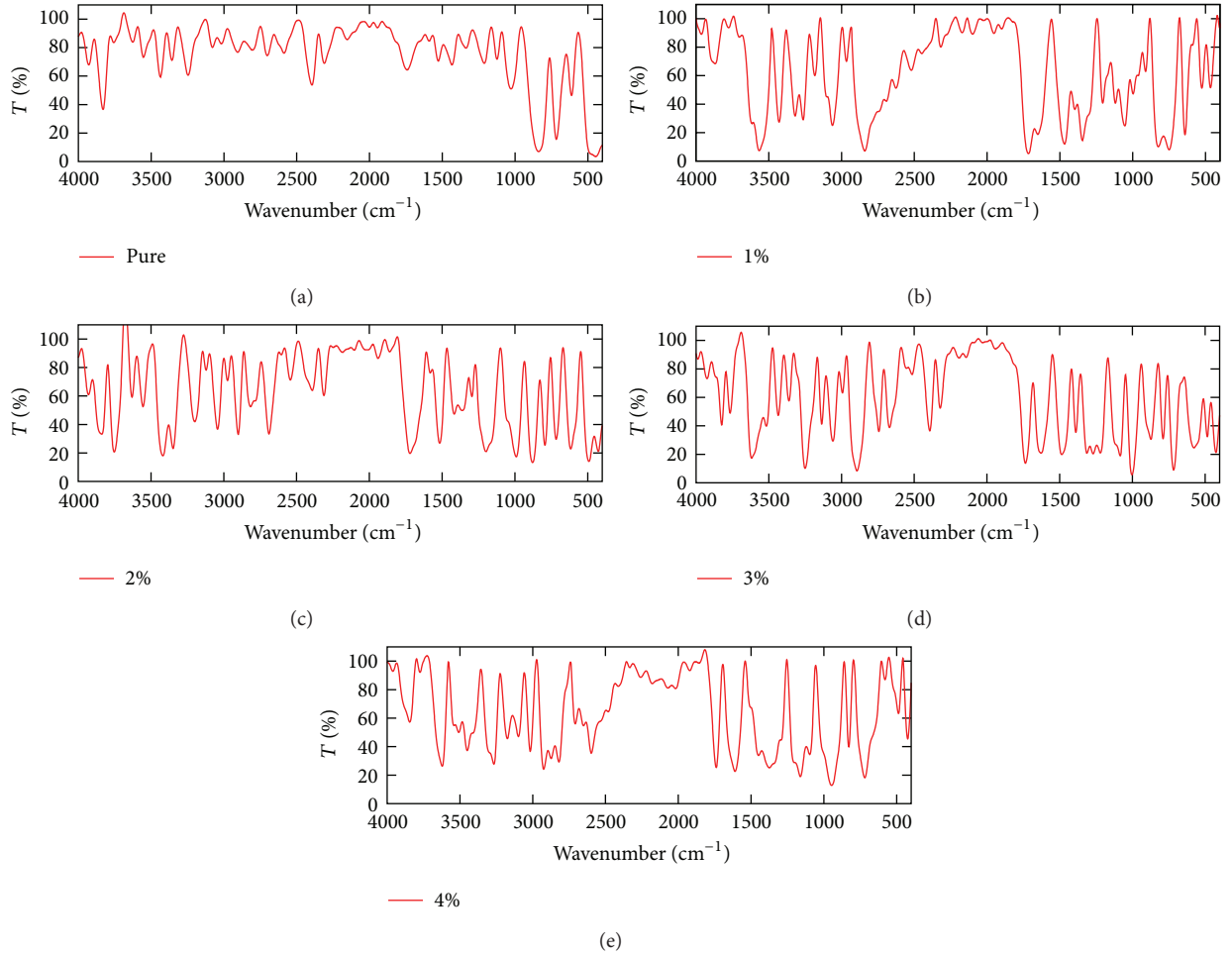
FIGURE 5: Variation of conductivity with frequency.

Frequency of the first overtone = 3830 cm^{-1}

$$= 2\bar{\nu}_e - 6\chi_e \bar{\nu}_e, \quad (3)$$

where $\bar{\nu}_e$ is the equilibrium vibration frequency and χ_e is the anharmonicity constant.

Solving these two equations, we get equilibrium vibration frequency and hence we can calculate anharmonicity constant. For pure PVA, the calculated equilibrium vibration

FIGURE 6: FTIR spectrum of pure PVA and various concentrations of CdCl_2 polymer films.TABLE 3: IR data of pure and CdCl_2 doped PVA polymer films.

Samples	Equilibrium vibration frequency ν_e (cm^{-1})	Anharmonicity constant χ_e (10^{-3})	ε_o (cm^{-1})	Force constant k (N/m)
Pure	2002	14.48	998.7	222.2
1% CdCl_2	1988	9.05	989.5	219.1
2% CdCl_2	1982	10.59	985.7	217.7
3% CdCl_2	1999	14.50	998.2	221.5
4% CdCl_2	1931	1.55	964.7	206.7

frequency and anharmonicity constant are 2002 cm^{-1} and 14.48×10^{-3} . The equilibrium vibration frequency decreases for various concentrations of CdCl_2 salt. Zero point energy is calculated for these samples using the following relation [16]:

$$\varepsilon_o = \frac{1}{2} \bar{\nu}_e \left(1 - \frac{\chi_e}{2} \right). \quad (4)$$

The zero point for pure PVA sample is 993.7 cm^{-1} and it decreases for various concentrations of CdCl_2 salt. The force constant for all the samples is calculated using the following relation:

$$k = 4\pi^2 \mu c^2 \bar{\nu}_e^2, \quad (5)$$

where μ is the reduced mass of the system and c is the velocity of light. The calculated force constant for pure PVA is 222.2 Nm^{-1} and it decreases for various concentrations of CdCl_2 salt. The calculated values of equilibrium vibration frequency, anharmonicity constant, zero point energy, and force constant for pure PVA and for various concentrations are tabulated as shown in Table 3. It is evident from Table 3 that equilibrium vibrational frequency, anharmonicity constant, force constant, and zero point energy decrease with increase in CdCl_2 . This is due to interaction of the dopant with the polymer chain mainly with the hydroxyl group as observed in FTIR spectrum which results in more amorphous structure.

4. Conclusion

Polymer blend electrolytes were prepared with PVA for different concentrations of CdCl_2 and we observe the highest conductivity of $1.68 \times 10^{-8} \text{ Scm}^{-1}$ using solution casting technique at room temperature. Such polymer electrolyte is suitable for storing devices like batteries and other applications. XRD studies show complete complexation of CdCl_2 salt in the polymer network. Furthermore, for the first time we have presented unit cell crystallite shape and crystallite sizes for different Bragg reflections. From this study, we observe that the conductivity and XRD results are complementary to each other. With concentration, conductivity at 1 kHz increases, whereas on average the crystallite area decreases. This is in conformity with the earlier studies [17] wherein the authors mention that this is due to the inversion centre in polymer network which is created by the inorganic molecule CdCl_2 which reduces the overall crystalline domains in these polymer blends. These polymer films are also suitable for the use in electrochemical applications. IR studies also support this view.

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